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On the accuracy of one-component pseudopotential spin-orbit calculations

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Improvements on current one-component extraction procedures of spin-orbit pseudopotentials are investigated for high accuracy computation of spin-orbit coupling energies. By means of the perturbation-theory formalism we first show that spin-orbit pseudopotentials, extracted at the one-component self-consistent-field level from a reference all-electron Dirac-Coulomb or Dirac-Coulomb-Breit calculation, include valence spin-orbit polarization and relaxation effects. As a consequence the use of these pseudopotentials in uncontracted spin-orbit configuration interaction (CI) with singles from the reference ground-state configuration gives rise to double counting of these spin-orbit effects. Two new methods that avoid such double counting have been investigated. The first, so-called "explicit" method, calculates explicitly, by means of a four-component spin-orbit CI, the double-counted spin-orbit effects and removes them from the pseudopotentials. Due to the nonadditivity of the core and valence spin-orbit effects as well as the so-called "pseudovariational collapse," this method is shown to be cumbersome. In the second "implicit" method the spin-orbit pseudopotential is extracted at the spin-orbit polarized and relaxed level by means of a single-excitation spin-orbit CI calculation. Atomic tests on iodine demonstrate the ability of the latter method to solve the double-counting problem. © *2005 American Institute of Physics*.
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I. INTRODUCTION

Atomic relativistic pseudopotentials (PPs) are nowadays used intensively in quantum chemical calculations. Their efficiency relies on two types of separation. The first one is the core-valence separation which enables an explicit treatment of the valence electrons only, the core being simulated by the PP. The second one is the separation of the relativistic effects into scalar [included in the so-called averaged relativistic effective potential (AREP)] and spin-orbit (SO) effects. The AREP is of high interest for electronic structure calculations on heavy elements since it can be treated in the usual spin-free formalism[1,2] and therefore allows for an accurate treatment of the electronic correlation with the same cost as a nonrelativistic calculation. In order to compute the spin-orbit coupling, the definition of a SOPP adapted to the AREP is then required. There are currently many extraction procedures of SOPPs as extensively discussed in Refs. 1 and 2. The present paper focuses on a recent hybrid one-component method proposed by some of the authors.[3] Using in the extraction procedure the ground-state total-energy splitting instead of the one-electron one (as usually done in fully shape-consistent procedures[1]), this method ensures, for example, in the doublet case, that the SOPP reproduces at the one-component self-consistent-field (SCF) level the total ground-state SO splitting of a reference all-electron four-component Dirac-Coulomb-Hartree-Fock (DC-HF) calculation. The advantages of such a method compared to fully energy-consistent ones[2] are discussed in Refs. 3 and 4. Let us underline that it can be generalized to the multiplet case and atomic tests on tellurium have shown that such hybrid SOPPs are as accurate as energy-consistent PPs.[4] Since the SO effects are treated self-consistently in a DC-HF calculation, the valence SO polarization and relaxation effects are automatically incorporated into the extracted SOPP and are therefore treated in an effective way in usual (contracted) SO-configuration-interaction (CI) methods.

However, the advent of faster computers and algorithms enables us nowadays to use larger basis sets and active spaces. Analyzing in perturbation theory the two-component SCF and SO-CI calculations (Sec. II), it appears that the valence SO polarization and relaxation effects, coming from the self-consistent treatment of the SO operator in a two-component approach, can be recovered in the one-component scheme by means of a single-excitations SO-CI. If those effects are in practice rather small for the early actinides, for example,[5] they can be, however, significant for the heavy main elements. Let us consider the particular case of thallium which has been investigated, for example, by

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Vallet *et al.*[6] with the energy-consistent relativistic pseudopotentials from Leininger *et al.*[7] and the corresponding core-polarization potential (CPP). At the one-component SCF level, the SO splitting of the ^2P ground state was found to be equal to 7334.4 cm^{-1}. Then the introduction of single excitations from the reference configuration $6s^26p$ into the SO-CI space gave a splitting of 7943.4 cm^{-1} which is significantly higher (by 609 cm^{-1}) than the SCF value. Therefore the combination of our current SOPPs with uncontracted SO-CI calculations[6] may lead to a non-negligible double-counting problem if singles from the reference ground-state configuration are included in the SO-CI space. This serious problem concerns in general the one-component extraction procedures of relativistic effective core potentials using as reference four-component DC total-energy splittings. A new definition of the SOPP, adapted to uncontracted SO-CI calculations, is then required. In the light of the analysis of usual two-component and hybrid one-component extraction procedures (Sec. III), two new hybrid one-component methods are proposed in Sec. IV. The first one called "explicit method" consists in calculating explicitly in the reference four-component calculation, by means of a DC-SO-CI, the effects of valence SO polarization and relaxation which may be double counted. Thus, the new SOPP is extracted from a reference total-energy splitting in which the latter effects have been removed. The second one called "implicit method" consists in adjusting the SOPP so that it reproduces at the single-excitation SO-CI level (using as reference space the ground-state configuration only) the SO splitting of the all-electron DC-HF calculation. Both of them are tested in the doublet case by performing SOPP calculations on the ground state of iodine (Sec. V). In Sec. VI a comparison of the usual two- and one-component extracted AREPs and their role in the SOPP calculation is finally proposed in the framework of the perturbation theory.

II. THEORY

In this section both two- and one-component quasirelativistic PP calculations are described in the framework of the perturbation theory using the diagrammatic formalism developed by Lindgren and Morrison[8] for open-shell systems. These theoretical derivations enable us to analyze in Sec. III the usual shape-consistent extraction procedures of relativistic pseudopotentials and to propose in Secs. IV A and IV B the improvements of our current hybrid one-component extraction of the SOPP for an accurate treatment of the SO coupling.

A. Perturbative analysis of two-component SCF pseudopotential calculations

In the two-component approach[3] the SO effects are taken into account in the SCF process. Adapting the formalism of Lindgren and Mårtensson to the pseudopotential calculations, the two-component Fock equation can be formulated as

$$h_P^{\mathrm{HF}}|j_P\rangle = \varepsilon_{j_P}|j_P\rangle, \tag{1}$$

where $h_P^{\mathrm{HF}}=p^2/2m-Z_{\mathrm{eff}}/r+u_P^{\mathrm{HF}}+U^{\mathrm{AREP}}+U^{\mathrm{SO}}$. The AREP ($U^{\mathrm{AREP}}$) containing the scalar relativistic effects and the SOPP (U^{SO}) containing the SO effects have the following form:

$$\begin{cases} U^{\mathrm{AREP}} = \sum_{l=0}^{+\infty} \sum_{m_l=-l}^{+l} \sum_{\sigma=\alpha,\beta} U_l^{\mathrm{AREP}}(r)|l,m_l,\sigma\rangle\langle l,m_l,\sigma| \\ U^{\mathrm{SO}} = \sum_{l=1}^{+\infty} \sum_{j=l-(1/2)}^{+l+(1/2)} \sum_{m_j=-j}^{+j} U_{l,j}^{\mathrm{SO}}(r)|l,j,m_j\rangle\langle l,j,m_j|, \end{cases} \tag{2}$$

and the two-component Fock potential u_P^{HF} (where P stands for Pauli) is defined as

$$\langle i|u_P^{\mathrm{HF}}|j\rangle = \sum_{a_P}^{\mathrm{holes}} \langle ia_P||ja_P\rangle, \tag{3}$$

where $\langle ia_P||ja_P\rangle=\langle ia_P|ja_P\rangle-\langle ia_P|a_Pj\rangle$.

If the SOPP U^{SO} is ignored at the SCF level (see Sec. II B), the two-component Fock operator h_P^{HF} is replaced by the scalar Fock operator $h_S^{\mathrm{HF}}=p^2/2m-Z_{\mathrm{eff}}/r+u_S^{\mathrm{HF}}+U^{\mathrm{AREP}}$ where S stands for scalar and u_S^{HF} denotes the scalar Fock potential which may differ from the two-component one u_P^{HF}. In the following, scalar hole and particle states $|j_S\rangle$ as well as their associated one-electron energy ε_{j_S} are simply denoted as $|j\rangle$ and ε_j.[9] Thus the scalar Fock potential is defined as

$$\langle i|u_S^{\mathrm{HF}}|j\rangle = \sum_{a}^{\mathrm{holes}} \langle ia||ja\rangle, \tag{4}$$

letting $|(j=l+\frac{1}{2})_P\rangle$ and $|(j=l-\frac{1}{2})_P\rangle$ be two Pauli hole states. In the so-called "hole problem," which enables us, for example, to describe the halogens in their ground-state configuration, a closed-shell state $|\alpha_P\rangle$ is built as

$$|\alpha_P\rangle = \prod_{a_P}^{\mathrm{holes}} a_{a_P}^{\dagger}|0\rangle, \tag{5}$$

$|0\rangle$ being the vacuum state. Applying excitation operators on $|\alpha_P\rangle$, a basis set for the atomic states can be generated. In the special case of single-hole atomic states $|(J=l\pm\frac{1}{2})_P\rangle$ defined in second quantization as

$$\left|\left(J=l\pm\tfrac{1}{2}\right)_P\right\rangle = a_{[j=l\pm(1/2)]_P}|\alpha_P\rangle, \tag{6}$$

the Koopmans theorem states that the total SO splitting $E_{\mathrm{SCF,SO}}^{2-\mathrm{cpt}}=E_{[J=l-(1/2)]_P}-E_{[J=l+(1/2)]_P}$ obtained at the two-component SCF level of calculation can be expressed as the difference between the fine-structure one-electron energies

$$E_{\mathrm{SCF,SO}}^{2-\mathrm{cpt}} = \varepsilon_{[j=l+(1/2)]_P} - \varepsilon_{[j=l-(1/2)]_P}. \tag{7}$$

Let us underline that in practical calculations the Koopmans theorem is not systematically fulfilled since the SCF spinors are usually optimized at the averaged level with the hole on the valence shell. This is extensively discussed in Ref. 3. For clarity we consider in this analysis the spinors optimized in the closed-shell case. The relaxation of these

spinors due to the valence-shell's hole will be recovered in the second-order contributions to the energy via single excitations.[10]

In the perturbative approach[9] the two-component Fock operator h_P^{HF} is rewritten as

$$h_P^{\mathrm{HF}} = h_S^{\mathrm{HF}} + v_1 + U^{\mathrm{SO}}, \tag{8}$$

considering as zeroth-order one-electron Hamiltonian the scalar Fock operator h_S^{HF} introduced previously. The v_1 operator corresponds to the difference between the two-component and the scalar Fock potentials

$$v_1 = u_P^{\mathrm{HF}} - u_S^{\mathrm{HF}}, \tag{9}$$

and the perturbation is $v_1 + U^{\mathrm{SO}}$. This way the Pauli one-electron states [solutions of Eq. (1)] and their associated one-electron energy can be derived, respectively, at the first and second orders of perturbation

$$\begin{cases} |j_P\rangle = |j\rangle + \sum_{\varepsilon_i \neq \varepsilon_j} \dfrac{|i\rangle\langle i|v_1 + U^{\mathrm{SO}}|j\rangle}{\varepsilon_j - \varepsilon_i} \\ \varepsilon_{jp} = \varepsilon_j + \langle v_1 + U^{\mathrm{SO}}\rangle_j + \sum_{\varepsilon_i \neq \varepsilon_j} \dfrac{\langle i|v_1 + U^{\mathrm{SO}}|j\rangle\langle j|v_1 + U^{\mathrm{SO}}|i\rangle}{\varepsilon_j - \varepsilon_i} \end{cases}. \tag{10}$$

Denoting $\{|r\rangle\}$ the scalar particle states and assuming that the scalar hole states are not coupled by the perturbation $v_1 + U^{\mathrm{SO}}$, the Pauli hole states are expressed according to Eq. (10) as

$$|a_P\rangle = |a\rangle + \sum_r \frac{|r\rangle\langle r|v_1 + U^{\mathrm{SO}}|a\rangle}{\varepsilon_a - \varepsilon_r}. \tag{11}$$

Thus the matrix elements of the two-component Fock potential can be reformulated, using Eq. (3) and taking into account the linear terms in U^{SO} and v_1 only, as

$$\langle i|u_P^{\mathrm{HF}}|j\rangle = \sum_a^{\mathrm{holes}} \langle ia||ja\rangle + \sum_a^{\mathrm{holes}} \sum_r \frac{\langle r|v_1 + U^{\mathrm{SO}}|a\rangle\langle ia||jr\rangle + \langle a|v_1 + U^{\mathrm{SO}}|r\rangle\langle ir||ja\rangle}{\varepsilon_a - \varepsilon_r}. \tag{12}$$

For any one-electron operator V, we define the $\mathbf{F}$ operator which associates with V the one-electron operator $\mathbf{F}(V)$ as follows:

$$\langle i|\mathbf{F}(V)|j\rangle = \sum_a^{\mathrm{holes}} \sum_r \frac{\langle r|V|a\rangle\langle ia||jr\rangle + \langle a|V|r\rangle\langle ir||ja\rangle}{\varepsilon_a - \varepsilon_r}. \tag{13}$$

Then, according to Eqs. (4), (9), and (12), v_1 is found to be the solution of the self-consistent equation

$$v_1 = \mathbf{F}(v_1) + \mathbf{F}(U^{\mathrm{SO}}). \tag{14}$$

Defining the series

$$\begin{cases} V^{n+1} = \mathbf{F}(V^n), \quad n \geqslant 0 \\ V^0 = U^{\mathrm{SO}} \end{cases}, \tag{15}$$

the v_1 operator can be written explicitly, according to Eq. (14), as

$$v_1 = \sum_{n=1}^{+\infty} V^n, \tag{16}$$

since

$$\mathbf{F}\left(\sum_{n=1}^{+\infty} V^n\right) = \sum_{n=1}^{+\infty} \mathbf{F}(V^n) = \sum_{n=1}^{+\infty} V^n - \mathbf{F}(U^{\mathrm{SO}}). \tag{17}$$

If we keep in Eq. (10) all linear terms as well as the quadratic terms in U^{SO} (which may contribute significantly[3]), the one-electron energy of the Pauli hole state $|m_P\rangle \in \{|(j = l \pm \frac{1}{2})_P\rangle\}$ introduced in Eq. (6) is developed in perturbation theory as follows:

$$\varepsilon_{mp} = \varepsilon_m + \langle U^{\mathrm{SO}} + v_1\rangle_m + \langle R\rangle_m, \tag{18}$$

where

$$R = \sum_{\varepsilon_i \neq \varepsilon_m} \frac{U^{\mathrm{SO}}|i\rangle\langle i|U^{\mathrm{SO}}}{\varepsilon_m - \varepsilon_i}. \tag{19}$$

Let us consider the second-order contributions to the so-called SO hole polarization terms $\langle v_1\rangle_m$. According to Eqs. (13), (15), and (16) they are deduced from the V^1 operator and can be written as

$$\langle V^1\rangle_m = \sum_a^{\mathrm{holes}} \sum_r \frac{\langle r|U^{\mathrm{SO}}|a\rangle\langle ma||mr\rangle + \langle a|U^{\mathrm{SO}}|r\rangle\langle mr||ma\rangle}{\varepsilon_a - \varepsilon_r}. \tag{20}$$

The corresponding Goldstone diagrams (1)-(4) are given in Fig. 1. The third-order SO hole polarization diagrams given in Figs. 2–4 can be derived in a very similar way from the V^2 operator. The so-called SO relaxation contributions $\langle R\rangle_m$ are graphically represented by diagrams (5-a) and (5-b) in Fig. 1.

Therefore the two-component SCF total SO splitting derived in Eq. (7) is, according to Eq. (18), developed in perturbation theory as

$$E_{\mathrm{SCF,SO}}^{2-\mathrm{cpt}} = E_{\mathrm{SO\ split.}} + E_{\mathrm{SO\ pol.}} + E_{\mathrm{SO\ relax.}}, \tag{21}$$

where we separate the SO energy splitting effects (first order), the SO hole polarization effects (second and higher orders), and the SO relaxation effects (second order), respectively, defined as follows:

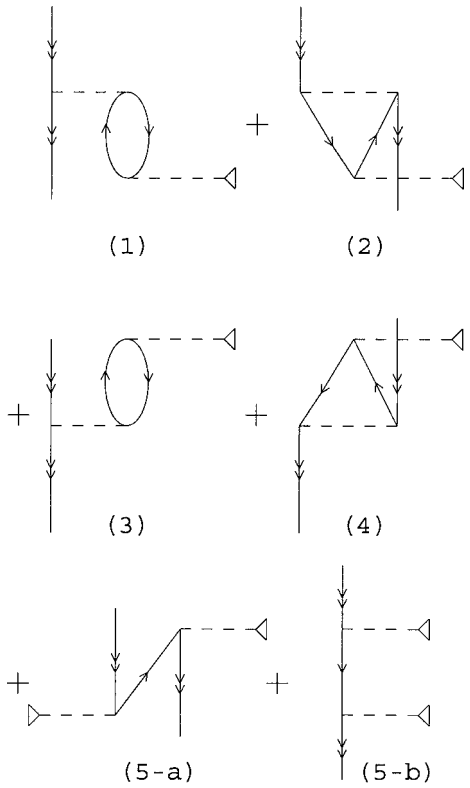

FIG. 1. Second-order spin-orbit hole polarization and relaxation diagrams for the "hole problem."

$$\begin{cases} E_{\text{SO split.}} = \langle U^{\text{SO}} \rangle_{j=l+(1/2)} - \langle U^{\text{SO}} \rangle_{j=l-(1/2)} \\ E_{\text{SO pol.}} = \langle \upsilon_1 \rangle_{j=l+(1/2)} - \langle \upsilon_1 \rangle_{j=l-(1/2)} \\ E_{\text{SO relax.}} = \langle R \rangle_{j=l+(1/2)} - \langle R \rangle_{j=l-(1/2)} \end{cases} . \tag{22}$$

The scalar hole states $|j=l+\frac{1}{2}\rangle$ and $|j=l-\frac{1}{2}\rangle$ are represented by Pauli spinors with the same radial part and associated with the same scalar one-electron energy ε_l. Introducing the l-dependent SOPP $U_l^{\text{SO}} = U_{l,j=l+(1/2)}^{\text{SO}} - U_{l,j=l-(1/2)}^{\text{SO}}$, $E_{\text{SO split.}}$ can then be reformulated, according to Eq. (2), as

$$E_{\text{SO split.}} = \langle U_l^{\text{SO}} \rangle_l . \tag{23}$$

Moreover, in the particular case of large core pseudopotentials, the diagram (5-b) in Fig. 1 is equal to zero so that the SO relaxation terms $\langle R \rangle_{j=l\pm(1/2)}$ can be simplified as follows:

$$\langle R \rangle_{j=l\pm(1/2)} = \sum_n^{\varepsilon_{n,l} > \varepsilon_l} \frac{|\langle n,l|U_{l,j=l\pm(1/2)}^{\text{SO}}|l\rangle|^2}{\varepsilon_l - \varepsilon_{n,l}} . \tag{24}$$

Since the fine-structure SOPPs fulfill[3] the equation

$$l U_{l,j=l-(1/2)}^{\text{SO}} + (l+1) U_{l,j=l+(1/2)}^{\text{SO}} = 0 , \tag{25}$$

the SO relaxation contribution to the total SO splitting is then equal to

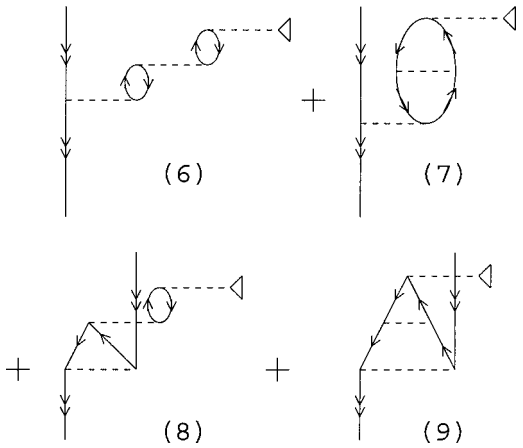

FIG. 2. Third-order spin-orbit hole polarization diagrams for the "hole problem" (first part).

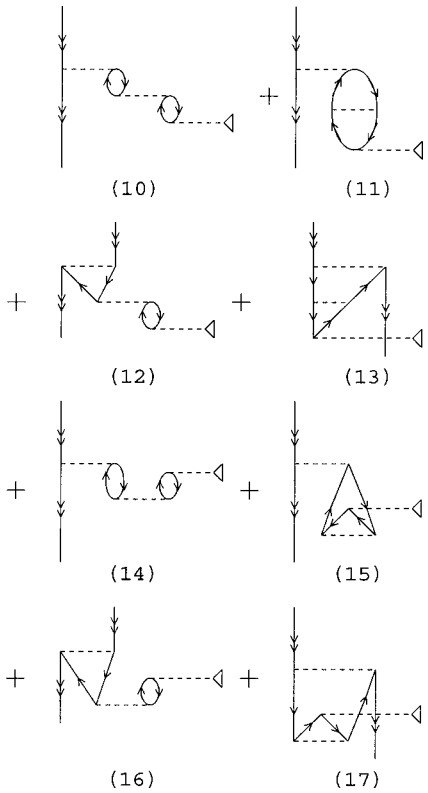

FIG. 3. Third-order spin-orbit hole polarization diagrams for the "hole problem" (second part).

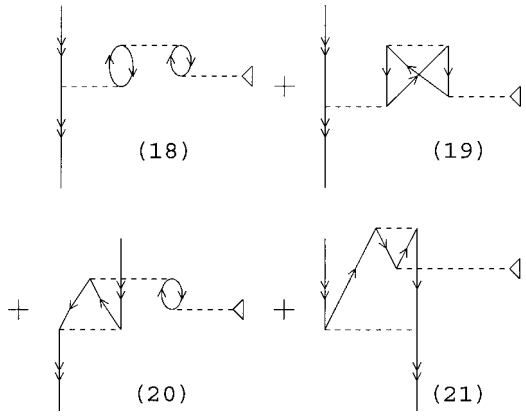

FIG. 4. "Ground-state correlation" (Ref. 8) diagrams for the "hole problem."

$$E_{\text{SO relax.}} = -\frac{1}{2l+1}\sum_{n}^{\varepsilon_{n,l}>\varepsilon_l}\frac{|\langle n,l|U_l^{\text{SO}}|l\rangle|^2}{\varepsilon_l-\varepsilon_{n,l}} > 0. \quad (26)$$

B. Perturbative analysis of spin-orbit CI calculations

In the one-component approach[3] the Fock equation

$$\left(\frac{p^2}{2m}-\frac{Z_{\text{eff}}}{r}+U^{\text{AREP}}+u_S^{\text{HF}}\right)|j\rangle=\varepsilon_j|j\rangle \quad (27)$$

is solved without taking into account the SOPP in the SCF process. In the framework of the perturbation theory, the SO effects as well as the correlation are then treated as a perturbation. Let us consider the hole problem extensively discussed in Ref. 3. At the one-component SCF level (first order of perturbation) the total SO splitting can be written as

$$E_{\text{SCF,SO}}^{1-\text{cpt}}=\langle U_l^{\text{SO}}\rangle_l, \quad (28)$$

which means that only SO energy splitting effects are considered at this level of calculation. At the second order of perturbation the SO hole polarization and relaxation diagrams of Fig. 1 are generated via single excitations from the reference configuration (see Figs. 1 and 3 in Ref. 3). As shown in Refs. 9 and 11 the third- (see Figs. 2–4) and higher-order SO hole polarization diagrams appear also in the energy perturbation development. Therefore the SO effects calculated at the two-component SCF level (energy splitting, hole polarization, and relaxation) can be recovered in the one-component scheme, provided single excitations are included in the SO-CI space.

III. USUAL SHAPE-CONSISTENT EXTRACTION PROCEDURES OF RELATIVISTIC PSEUDOPOTENTIALS

This section is devoted to the critical analysis of usual shape-consistent two-component and our recent hybrid one-component extraction procedures of relativistic pseudopotentials[3] by means of the perturbation-theory formalism developed in Sec. II. Improvements of our current method are then investigated for an accurate pseudopotential calculation of the SO polarization and relaxation effects.

A. Two-component procedure

In the two-component procedure the fine-structure PPs $\{U_{l,j}^{\text{REP(2)}}\}_{l,j=|l\pm(1/2)|}$ which contain both scalar and SO effects and define the relativistic PP $U^{\text{REP(2)}}$ as follows:

$$U^{\text{REP(2)}}=\sum_{l=0}^{+\infty}\sum_{j=|l-(1/2)|}^{j=l+(1/2)}\sum_{m_j=-j}^{+j}U_{l,j}^{\text{REP(2)}}(r)|l,j,m_j\rangle\langle l,j,m_j| \quad (29)$$

are determined in order to reproduce at the two-component SCF level the one-electron fine-structure energies $\varepsilon_{j=|l\pm(1/2)|}^{\text{ref}}$ of the reference all-electron four-component Dirac-Hartree-Fock calculation

$$\left(\frac{p^2}{2m}-\frac{Z_{\text{eff}}}{r}+U_{l,j}^{\text{REP(2)}}+u_P^{\text{HF}}\right)|j_P\rangle=\varepsilon_j^{\text{ref}}|j_P\rangle. \quad (30)$$

In the present work a Dirac-Coulomb-Hartree-Fock (DC-HF) calculation has been used as a reference which means that the Breit interaction has been neglected. Nevertheless, the discussion would be the same with a reference Dirac-Coulomb-Breit-Hartree-Fock (DCB-HF) calculation.

Let us rewrite $U_{l,j=|l\pm(1/2)|}^{\text{REP(2)}}$ as

$$U_{l,j=|l\pm(1/2)|}^{\text{REP(2)}}=U_l^{\text{AREP(2)}}+U_{l,j=|l\pm(1/2)|}^{\text{SO(2)}}, \quad (31)$$

where the scalar and the SO terms are equal to

$$\begin{cases} U_l^{\text{AREP(2)}}=\dfrac{lU_{l,j=|l-(1/2)|}^{\text{REP(2)}}+(l+1)U_{l,j=l+(1/2)}^{\text{REP(2)}}}{2l+1} \\ U_{l,j=|l\pm(1/2)|}^{\text{SO(2)}}=\pm\dfrac{\left(l+\frac{1}{2}\mp\frac{1}{2}\right)}{2l+1}(U_{l,j=l+(1/2)}^{\text{REP(2)}}-U_{l,j=|l-(1/2)|}^{\text{REP(2)}}) \end{cases}. \quad (32)$$

Thus, according to Eqs. (29) and (31), the relativistic PP can be written as the sum of an AREP and a SOPP extracted via a two-component procedure

$$U^{\text{REP(2)}}=U^{\text{AREP(2)}}+U^{\text{SO(2)}}. \quad (33)$$

Therefore Eq. (30) is formally equivalent to Eq. (1) which implies, according to Eq. (7), that the total SO splitting obtained for the hole problem at the two-component SCF level with $U^{\text{REP(2)}}$ is $E_{\text{SCF,SO}}^{2-\text{cpt(2)}}=\varepsilon_{j=l+(1/2)}^{\text{ref}}-\varepsilon_{j=l-(1/2)}^{\text{ref}}$. For consistency reasons we assume (Sec. II A) that the one-electron energies $\varepsilon_{j=|l\pm(1/2)|}^{\text{ref}}$ are obtained from a closed-shell DC-HF calculation. In this case the DC-HF total SO splitting is equal, according to the Koopmans theorem, to

$$E_{\text{DC-HF,SO}}^{\text{ref}}=\varepsilon_{j=l+(1/2)}^{\text{ref}}-\varepsilon_{j=l-(1/2)}^{\text{ref}}, \quad (34)$$

so that

$$E_{\text{SCF,SO}}^{2-\text{cpt(2)}}=E_{\text{DC-HF,SO}}^{\text{ref}}. \quad (35)$$

The two-component procedure ensures that the total SO splitting of the reference DC-HF calculation is reproduced at the two-component SCF level which is well founded since in both cases the SO effects are treated self-consistently.

In order to compare the two- and one-component procedures it is of high interest to formulate an extraction condition for $U^{\text{AREP(2)}}$ and $U^{\text{SO(2)}}$ from the definition (30). According to Eq. (18) we have in perturbation theory

$$\varepsilon_{j=l\pm(1/2)}^{\text{ref}}=\varepsilon_l^{(2)}+\langle U_{l,j=l\pm(1/2)}^{\text{SO(2)}}\rangle_l+\langle v_1^{(2)}\rangle_{j=l\pm(1/2)}+\langle R^{(2)}\rangle_{j=l\pm(1/2)}, \quad (36)$$

where $\varepsilon_l^{(2)}$ is the scalar one-electron energy generated by the AREP $U^{\text{AREP(2)}}$. By Landé averaging and difference we finally get according to Eqs. (22) and (25)

$$\begin{cases} \varepsilon_l^{(2)} = \dfrac{l\varepsilon^{\text{ref}}_{j=l-(1/2)} + (l+1)\varepsilon^{\text{ref}}_{j=l+(1/2)}}{2l+1} - \dfrac{l\langle v_1^{(2)} + R^{(2)}\rangle_{j=l-(1/2)} + (l+1)\langle v_1^{(2)} + R^{(2)}\rangle_{j=l+(1/2)}}{2l+1} \\ \langle U_l^{\text{SO}(2)}\rangle_l = E^{\text{ref}}_{\text{DC-HF,SO}} - E^{(2)}_{\text{SO pol.}} - E^{(2)}_{\text{SO relax.}} \end{cases} \tag{37}$$

B. Hybrid one-component procedure

The one-component procedure consists in extracting separately the AREP $U^{\text{AREP}(1)}$ and the SOPP $U^{\text{SO}(1)}$ in order to get the full relativistic PP $U^{\text{REP}(1)} = U^{\text{AREP}(1)} + U^{\text{SO}(1)}$. In the particular case of the "hole problem" considered in this paper, they are optimized[3] in order to fulfill

$$\begin{cases} \varepsilon_l^{(1)} = \dfrac{l\varepsilon^{\text{ref}}_{j=l-(1/2)} + (l+1)\varepsilon^{\text{ref}}_{j=l+(1/2)}}{2l+1} \\ \langle U_l^{\text{SO}(1)}\rangle_l = E^{\text{ref}}_{\text{DC-HF,SO}} \end{cases}, \tag{38}$$

where $\varepsilon_l^{(1)}$ is the scalar one-electron energy generated at the scalar SCF level

$$\left(\frac{p^2}{2m} - \frac{Z_{\text{eff}}}{r} + U_l^{\text{AREP}(1)} + u_S^{\text{HF}}\right)|l\rangle = \varepsilon_l^{(1)}|l\rangle. \tag{39}$$

This procedure is called "hybrid" since the SOPP definition involves a pseudo-orbital (shape consistent[1]) and the total SO splitting $E^{\text{ref}}_{\text{DC-HF,SO}}$ (energy consistent[2]) which may differ in practical calculations from the one-electron one $\varepsilon^{\text{ref}}_{j=l+(1/2)} - \varepsilon^{\text{ref}}_{j=l-(1/2)}$.[3]

According to Eqs. (28) and (38), the one-component SCF total SO splitting obtained with $U^{\text{AREP}(1)}$ and $U^{\text{SO}(1)}$ is

$$E^{1-\text{cpt}(1)}_{\text{SCF,SO}} = E^{\text{ref}}_{\text{DC-HF,SO}}. \tag{40}$$

At this level of calculation the SOPP is treated at the first order of perturbation which means that the SO energy splitting effects only are taken into account. However, since the reference DC-HF calculation treats the SO effects self-consistently, we can deduce from Sec. II A that $E^{\text{ref}}_{\text{DC-HF,SO}}$ contains already the SO hole polarization and relaxation effects. The current one-component procedure is therefore well founded if the extracted PPs are used in contracted SO-CI calculations[1] which do not calculate those effects. In this case the SOPP is extracted following an "effective Hamiltonian" approach which consists in including in the energies the SO hole polarization and relaxation effects but not in the wave function. In practice contracted SO-CI approaches are found to be quite accurate for the early actinides[5] but not for heavy main elements[3,6] which require a better treatment of the SO coupling. Introducing in the SO-CI space single excitations from the reference configuration, it is possible (Sec. II B) to mimic in a one-component scheme the two-component SCF calculation which increases significantly the accuracy of the SO calculations.[6] This can be done, for example, with the EPCISO code.[6] In this case the effective Hamiltonian approach used to define the current SOPP $U^{\text{SO}(1)}$ is not valid anymore since the valence SO polarization and relaxation effects are calculated explicitly. In other words using $U^{\text{SO}(1)}$ with EPCISO leads to double-counting problems. This appears clearly if we perform a two-component SCF calculation with the relativistic PP $U^{\text{REP}(1)}$. According to Eqs. (21), (23), and (38) the total SO splitting obtained at this level of calculation for the hole problem is equal to

$$E^{2-\text{cpt}(1)}_{\text{SCF,SO}} = E^{\text{ref}}_{\text{DC-HF,SO}} + E^{(1)}_{\text{SO pol.}} + E^{(1)}_{\text{SO relax.}}. \tag{41}$$

Therefore, in the particular case of large core PPs, we may overestimate the expected value $E^{\text{ref}}_{\text{DC-HF,SO}}$ since according to Eq. (26) $E^{(1)}_{\text{SO relax.}} > 0$.

IV. EXTRACTION OF UNCONTRACTED SO-CI-ADAPTED SOPPS

In order to solve the double-counting problems which occur when current hybrid one-component extracted SOPPs are used in uncontracted SO-CI calculations (with single excitations), we propose and discuss two new possible extraction procedures. The first one presented in Sec. IV A consists in deleting from the reference calculation the SO effects which may be double counted and then in extracting the SOPP at the one-component SCF level. Another possibility presented in Sec. IV B consists in keeping, as reference total SO splitting, the DC-HF one and extracting the SOPP at the one-component SO-polarized and -relaxed level of calculation. In this case a post-SCF treatment is required.

A. Separation of scalar and spin-orbit effects in the reference four-component calculation

The hybrid one-component SCF extraction (38) gives an explicit definition of the SOPP and is in this respect more straightfoward than fully energy-consistent procedures. In order to avoid the double-counting problems mentioned in Sec. III B, it could be adapted to uncontracted SO-CI calculations as follows:[3]

$$\begin{aligned} &\langle U_l^{\text{SO}(1)}\rangle_l = E^{\text{ref}}_{\text{DC-HF,SO}} \\ &\quad \rightarrow \langle U^{\text{SO}(1)}_{\text{explicit},l}\rangle_l = E^{\text{ref}}_{\text{DC-HF,SO}} - E^{\text{ref}}_{\text{val.SO pol.+relax.}}, \end{aligned} \tag{42}$$

where $E^{\text{ref}}_{\text{val.SO pol.+relax.}}$ denotes the contribution of the valence SO polarization and relaxation effects to the reference DC-HF total SO splitting.

One possibility to compute $E^{\text{ref}}_{\text{val.SO pol.+relax.}}$ consists in performing a four-component SO-CI, as implemented in the DIRAC package.[12]

Let us consider as case study the iodine atom, in its ground-state configuration $5s^2 5p^5$, and apply the perturbative analysis of Sec. II B to the all-electron four-component SO-CI case. At the second order of perturbation (Fig. 1) the nonzero terms come from single excitations $5p \rightarrow np (n > 5)$

TABLE I. Total SO splitting E_{SO} obtained for iodine via a four-component single-excitation DC-SO-CI and a DC-HF calculation. X_u and X_g denote the energy of the highest occupied virtual bispinor in the SO-CI space, respectively, for the *ungerade* symmetry $(p,f,\ldots)$ and the *gerade* symmetry $(s,d,\ldots)$.

Calculation	Active space (singles)	X_u (a.u.)	X_g (a.u.)	$E_{SO}(cm^{-1})$
SFDC-PT1	⋯	0	0	7056.19
DC-SO-CI	$5p$	10	0	7227.46
		10^2	0	7454.63
		10^3	0	7776.00
		10^4	0	8013.48
DC-SO-CI	$5p5s$	10^4	10	7870.88
DC-SO-CI	$5p5s4d4p4s3p2p$	10^4	10	7794.74
DC-HF	⋯	0	0	7765.76

and correspond to the valence SO relaxation. At the third order those singles reappear (Fig. 2) as well as single excitations $5s\rightarrow ns, 5s\rightarrow np$, and $5p\rightarrow ns$ with $n>5$ (Fig. 3), all of them contributing to the valence SO polarization. Therefore, assuming that the considered SO effects are additive like in perturbation theory, which is not obvious as will be discussed in Sec. V, we get the formula

$$E^{ref}_{val.SO\ pol.+relax.} = E^{ref}_{SO-CIS\ 5s5p,SO} - E^{ref}_{SFDC-PT1,SO}, \qquad (43)$$

where $E^{ref}_{SO-CIS\ 5s5p,SO}$ denotes the total SO splitting obtained from the four-component single-excitation SO-CI with the active space $5s5p$ and $E^{ref}_{SFDC-PT1,SO}$ the total SO splitting obtained at the first order of perturbation using spin-free-Dirac-Coulomb (SFDC) Hartree-Fock bispinors.

Let us underline that performing with DIRAC a four-component SO-CI with singles from the valence and core shells we almost recover the DC-HF total SO splitting (Table I) which is consistent with our perturbative analysis. Nevertheless, for valence-only SO-CI calculations, the SO splitting has been found very sensitive to the virtual space (Table I). This was already noticed by Visscher and Saue[12] for heavy atoms such as thallium and explained as a "pseudovariational collapse." In this respect this procedure may not be very safe to solve the double-counting problem. The atomic results for iodine are presented in Table III and discussed in Sec. V.

B. Extraction of the spin-orbit pseudopotential via a SO-CIS procedure

Another way to solve the double-counting problem consists in taking into account the valence SO polarization and relaxation effects in the extraction procedure. The SOPP is in this case determined so that it reproduces at the one-component SO-CIS level (with singles from the reference ground-state configuration only) the DC-HF total SO splitting. Thus the explicit definition (38) of the SOPP is changed into an implicit one as follows:

$$\langle U_l^{SO(1)}\rangle_l = E^{ref}_{DC-HF,SO} \rightarrow \langle U^{SO(1)}_{implicit,l}\rangle_l = E^{ref}_{DC-HF,SO} - E^{(1)}_{SO\ pol.}(U^{SO(1)}_{implicit}) - E^{(1)}_{SO\ relax.}(U^{SO(1)}_{implicit}). \qquad (44)$$

The advantage of this procedure compared to the previous one (Sec. IV A) lies in the complete control of the valence SO polarization and relaxation effects in the PP calculation. Moreover it can be generalized easily to the multiplet case. The only drawback lies on the fact that the SOPP can no longer be extracted at the one-component SCF level which makes the procedure less straightforward. This new method has been tested for iodine. The results are presented in Table III and discussed in Sec. V.

TABLE II. SOPPs extracted for iodine. All of them have the form $U_l^{SO}(r) = C_l^{SO} e^{-\alpha_l^{SO} r^2}$.

Extraction method	l	α_l^{SO}	C_l^{SO}
Explicit	1	2.433 041 30	10.618 919 28
Implicit	1	2.433 041 30	11.170 200 00
⋯	2	1.178 306 90	0.538 238 55

V. ATOMIC RESULTS FOR IODINE

The validity of our new uncontracted SO-CI-adapted SOPP extraction procedures presented in Sec. IV has been checked in the doublet case by performing SOPP calculations on the ground state of iodine using the EPCISO code.[6] The adapted scalar relativistic PP $U^{AREP(1)}$ (used to compute the spin-free states) as well as the corresponding basis set are given in Ref. 10. The exponent 0.65 has been added to the p functions in order to reproduce very accurately the reference SO splittings at the one-component SCF level. The extracted SOPPs are given in Table II and the results presented in Table III.

Let us first consider the explicit method introduced in Sec. IV A. As a first step in the extraction procedure, we performed different four-component DC-SO-CI calculations[12] in order to evaluate explicitly the valence SO polarization and relaxation effects which have to be deleted from our current hybrid one-component extracted SOPP, in

TABLE III. Comparison of the total SO splittings E_{SO} calculated for iodine at the SO-CI level (using current, explicitly and implicitly extracted SOPPs) and at the four-component all-electron level.

Extraction method	Code	SO calculation	$E_{SO}(cm^{-1})$
Current	MOLPRO	SCF (1 conf)	7764.60
		AQCC	7366.05
		AQCC+U_d^{SO}	7379.68
Explicit	EPCISO	SCF (1 conf)	6984.80
		1 conf+singles	7354.16
		43 confs (no singles)	6642.20
Implicit	EPCISO	SCF (1 conf)	7347.42
		1 conf+singles	7765.78
		43 confs (no singles)	6987.11
		43 confs+singles	7264.92
		43 confs+singles+U_d^{SO}	7347.81
⋯	DIRAC	DC-HF	7765.76
⋯	DIRAC	DC-CISD $5p5s$	7456.68
Expt. [a]			7603.00

[a]Reference 16.

order to avoid double-counting problems. The DIRAC package[13] was used as well as the pVTZ basis set of Dyall.[14] First, we computed the SO splitting at the SFDC first order of perturbation level (line "SFDC-PT1" in Table I) and found 7056.19 cm^{-1}. Secondly we introduced in the SO-CI space single excitations from the valence shells $5p$ and $5s$ (line "DC-SO-CI $5p5s$" in Table I) which gave as SO splitting 7870.88 cm^{-1}. Thus we found the valence SO polarization and relaxation effects within this procedure to be equal to $7870.88-7056.19=814.69$ cm^{-1}. Finally, in order to check the efficiency of the DC-SO-CIS, we considered singles from valence and core shells (line "DC-SO-CI $5p5s4d4p4s3p2p$" in Table I). In this case we got 7794.74 cm^{-1} and therefore almost recovered the DC-HF SO splitting as suggested by the perturbative analysis of Sec. II B. As a second step, the SOPP has been adjusted in order to reproduce at the one-component SCF level a SO splitting of $7794.74-814.69=6980.05$ cm^{-1}. If we now consider the SOPP calculation performed with this SOPP, we notice in Table III that this condition is fulfilled. Including then singles from the ground-state configuration $5s^25p^5$ in the PP SO-CI space, the SO splitting becomes equal to 7354.16 cm^{-1} which is smaller by 411.60 cm^{-1} than the expected DC-HF value. The explicitly extracted SOPP appears unable to calculate properly the valence SO polarization and relaxation effects. The basis set could be one of the reasons. Nevertheless atomic tests have shown that the one we used is large enough to describe correctly excited states.[10] The reference valence-only four-component DC-SO-CI calculation could be another reason. In fact, the SO splitting was found to be very sensitive to the virtual space (see Table I), as already noticed for thallium.[12] This so-called pseudovariational collapse is due to the fact that the SO-polarized and -relaxed valence bispinors are kept orthogonal to the core SFDC-HF bispinors in a valence-only DC-SO-CIS calculation whereas they should be orthogonal to the true DC-HF core bispinors. A four-component DC-SO-CI calculation should therefore include excitations from core and valence shells to be reliable. Another reason could be the nonadditivity of the considered SO effects. We calculated the SO polarization and relaxation effects on the valence shell in the field of SFDC-HF core bispinors and assumed that they were equal to the same effects calculated in the field of DC-HF core bispinors which is not obvious at all. A possible improvement to this method would consist in deleting (by projection, for example) from the four-component DC-SO-CIS with the active space $5p5s4d4p4s3p2p$ all the single excitations involving the valence shell and extract a SOPP with the corresponding SO splitting.

The other alternative consists in extracting the SOPP implicitly (Sec. IV B). In this case the SOPP is adjusted so that the SO splitting calculated at the PP single-excitation SO-CI level (using for the reference space the ground-state configuration $5s^25p^5$ only) is equal to the DC-HF one. The implicitly extracted SOPP thus improves upon the explicitly extracted SOPP, because it by construction takes care of the double-counting problem mentioned above (compare the lines marked "1 conf+singles" to the reference DC-HF result in Table III). Let us moreover notice that such a SOPP gives at the one-component SCF level a SO splitting of 7347.42 cm^{-1} (see Table III) which enables us to estimate the contribution of the valence SO polarization and relaxation effects around 418 cm^{-1} which is significant. Adding then the electronic correlation effects (line "43 confs+singles" in Table III) the SO splitting is equal to 7264.92 cm^{-1}. At this level, only the scalar PP U_d^{AREP} was used to treat the correlation effects. In principle a corresponding SOPP U_d^{SO} should be defined in order to ensure an accurate treatment of the fine-structure correlation terms that is, in perturbation theory, all the correlation diagrams calculated with the SO-polarized and -relaxed spinors. As a straightforward definition we optimized U_d^{SO} so that $\langle U_d^{\mathrm{SO}}\rangle_{\phi_d'}=\varepsilon_{d_{5/2}}^{\mathrm{ref}}-\varepsilon_{d_{3/2}}^{\mathrm{ref}}$ where ϕ_d', $\varepsilon_{d_{5/2}}^{\mathrm{ref}}$ and $\varepsilon_{d_{3/2}}^{\mathrm{ref}}$ are, respectively, the averaged pseudo-orbital and the one-electron fine-structure energies which were used for the extraction of U_d^{AREP}.[10] As shown in Table III (line "43 confs+singles+U_d^{SO}"), U_d^{SO} enables us to increase by 82.89 cm^{-1} the previous SO splitting which gives as a final result 7347.81 cm^{-1}. Let us first underline that this value is rather close to the SO splitting computed with MOLPRO and the current SOPP (Ref. 3) where the SO polarization and relaxation effects are treated in an effective way (line "AQCC+U_d^{SO}" in Table III). Secondly, it is found to be smaller by 108.87 cm^{-1} than the expected value of 7456.68 cm^{-1} obtained from the all-electron four-component DC-CISD calculation with the active space $5p5s$ (line "DC-CISD $5p5s$" in Table III).

If a high accuracy is desired in the computation of the SO coupling another definition of the correlation SOPP U_d^{SO} should be investigated, as mentioned previously. Moreover a detailed analysis of the excitations generated by EPCISO would be required in order to ensure an accurate treatment of the fine-structure correlation effects. Finally, the incorporation of the atomic core effects into the SOPP (Refs. 3 and 10) would be required in order to reach the experimental SO splitting. Let us keep in mind, however, that our implicit method is basis set dependent. So, even if the previous improvements are achieved, the influence of the basis set still needs to be carefully analyzed.

VI. ONE-VERSUS TWO-COMPONENT EXTRACTION OF RELATIVISTIC PSEUDOPOTENTIALS

The atomic tests performed on iodine demonstrate the validity of our new uncontracted SO-CI-adapted implicit hybrid one-component extraction of the SOPP. Nevertheless, for high accuracy SOPP one-component calculations, some improvements could be investigated. The first one, mentioned in Sec. V, concerns the SO-CI calculation itself which could be improved in order to calculate more precisely the fine-structure correlation contributions to the SO splitting. A second one, also mentioned in Sec. V, is the definition of a SOPP U_d^{SO} devoted to the accurate treatment of the fine-structure correlation. The third one concerns the AREP. According to Eqs. (37) and (38) the difference between the scalar one-electron energies, generated by the two- ($U^{\mathrm{AREP}(2)}$) and one-component ($U^{\mathrm{AREP}(1)}$) extracted AREPs at the one-component SCF level, is expressed as follows:

$$\varepsilon_l^{(1)} - \varepsilon_l^{(2)} = \frac{l\langle v_1^{(2)} + R^{(2)}\rangle_{j=l-(1/2)} + (l+1)\langle v_1^{(2)} + R^{(2)}\rangle_{j=l+(1/2)}}{2l+1}. \tag{45}$$

Rewriting with Eqs. (24) and (25) the Landé average of the valence SO relaxation terms as

$$\frac{l\langle R^{(2)}\rangle_{j=l-(1/2)} + (l+1)\langle R^{(2)}\rangle_{j=l+(1/2)}}{2l+1} = \frac{l(l+1)}{(2l+1)^2}\sum_n^{\varepsilon_{n,l}>\varepsilon_l} \frac{|\langle n,l|U_l^{\mathrm{SO}(2)}|l\rangle|^2}{\varepsilon_l - \varepsilon_{n,l}} < 0, \tag{46}$$

we finally deduce that $U^{\mathrm{AREP}(2)}$ differs from $U^{\mathrm{AREP}(1)}$. Let us notice that in Eq. (45) the Landé average of the valence SO polarization and relaxation terms is l dependent which implies that the spectra of $U^{\mathrm{AREP}(1)}$ and $U^{\mathrm{AREP}(2)}$ do not differ from a simple global shift.

Since the SO effects are treated self-consistently in the reference DC-HF calculation, the Landé averaging of the reference valence fine-structure one-electron energies kills the SO energy splitting effects (first order) but not the valence SO polarization and relaxation effects (second and higher orders) which means that $\varepsilon_l^{(1)}$ is not purely scalar. This was already noticed numerically by Leininger *et al.*[7] when extracting relativistic energy-consistent PPs. In the particular case of thallium, for example, a positive shift[15] was introduced into the SOPP in order to recover from the Landé average of the total DC-HF fine-structure energies the scalar-relativistic all-electron energy. Let us underline that this procedure was qualified as "unphysical" by the authors. If we consider in the present perturbative analysis the use of large core PPs for thallium then $v_1=0$ (since the core orbitals are s orbitals) so that $\varepsilon_l^{(1)} < \varepsilon_l^{(2)}$ according to Eqs. (45) and (46). The positive shift is therefore the absolute value of the SO relaxation terms Landé average and has, in this respect, a physical meaning.

If $U^{\mathrm{AREP}(1)}$ is used in a contracted SO-CI then its definition, as well as $U^{\mathrm{SO}(1)}$ definition, seems well founded. However, using $U^{\mathrm{AREP}(1)}$ in an uncontracted SO-CI calculation with singles might lead to double-counting problems even if our new SOPP $U_{\mathrm{implicit}}^{\mathrm{SO}(1)}$ is used. This appears clearly if we perform a two-component SCF calculation with the relativistic PP $U_{\mathrm{implicit}}^{\mathrm{REP}(1)} = U^{\mathrm{AREP}(1)} + U_{\mathrm{implicit}}^{\mathrm{SO}(1)}$. According to Eqs. (18), (38), and (39) the fine-structure one-electron energies generated at this level of calculation are

$$\varepsilon_{\mathrm{implicit},j=l\pm(1/2)}^{2-\mathrm{cpt}(1)} = \frac{l\varepsilon_{j=l-(1/2)}^{\mathrm{ref}} + (l+1)\varepsilon_{j=l+(1/2)}^{\mathrm{ref}}}{2l+1} + \langle U_{\mathrm{implicit}}^{\mathrm{SO}(1)} + v_{1,\mathrm{implicit}}^{(1)} + R_{\mathrm{implicit}}^{(1)}\rangle_{j=l\pm(1/2)}. \tag{47}$$

Rewriting with the Eq. (25) the SO energy splitting terms as

$$\langle U_{\mathrm{implicit}}^{\mathrm{SO}(1)}\rangle_{j=l\pm(1/2)} = \pm\frac{\left(l+\frac{1}{2}\mp\frac{1}{2}\right)}{2l+1}\langle U_{\mathrm{implicit},l}^{\mathrm{SO}(1)}\rangle_l, \tag{48}$$

and reformulating, according to Eqs. (22) and (34), the implicit definition of the SOPP (44) as follows:

$$\langle U_{\mathrm{implicit},l}^{\mathrm{SO}(1)}\rangle_l = (\varepsilon_{j=l+(1/2)}^{\mathrm{ref}} - \varepsilon_{j=l-(1/2)}^{\mathrm{ref}}) - (\langle v_{1,\mathrm{implicit}}^{(1)}\rangle_{j=l+(1/2)} - \langle v_{1,\mathrm{implicit}}^{(1)}\rangle_{j=l-(1/2)}) - (\langle R_{\mathrm{implicit}}^{(1)}\rangle_{j=l+(1/2)} - \langle R_{\mathrm{implicit}}^{(1)}\rangle_{j=l-(1/2)}), \tag{49}$$

the one-electron energies $\varepsilon_{\mathrm{implicit},j=l\pm(1/2)}^{2-\mathrm{cpt}(1)}$ can be expressed as

$$\varepsilon_{\mathrm{implicit},j=l\pm(1/2)}^{2-\mathrm{cpt}(1)} = \varepsilon_{j=l\pm(1/2)}^{\mathrm{ref}} + \frac{l\langle v_{1,\mathrm{implicit}}^{(1)} + R_{\mathrm{implicit}}^{(1)}\rangle_{j=l-(1/2)} + (l+1)\langle v_{1,\mathrm{implicit}}^{(1)} + R_{\mathrm{implicit}}^{(1)}\rangle_{j=l+(1/2)}}{2l+1}. \tag{50}$$

It appears that they differ from the expected values $\varepsilon_{j=l\pm(1/2)}^{\mathrm{ref}}$ given by $U^{\mathrm{REP}(2)}$.

Therefore, even if $U^{\mathrm{AREP}(1)}$ and $U_{\mathrm{implicit}}^{\mathrm{SO}(1)}$ reproduce at the two-component SCF level the DC-HF total SO splitting, one cannot ensure that they are well defined for an accurate treatment of the fine-structure correlation effects. Let us remind that in perturbation theory the difference of total scalar energies appears in the denominators of the second- and higher-orders contributions, which means that a proper definition of the SOPP is not enough for accurate SOPP calculations. The AREP generates the spin-free states which are used in the SO-CI. It is then as important as the SOPP for the calculation of the SO coupling. In this respect the two-component extraction procedure seems to be more adapted to high accuracy SO calculations than the one-component one.

Nevertheless, we should keep in mind that the present analysis assumes $U^{\mathrm{AREP}(1)}$ and $U^{\mathrm{REP}(2)}$ able to reproduce at the SCF level the full set of reference one-electron energies (occupied and virtual), $\{l\varepsilon_{n,j=l-(1/2)}^{\mathrm{ref}} + (l+1)\varepsilon_{n,j=l+(1/2)}^{\mathrm{ref}}/(2l+1)\}_{n,l}$ and $\{\varepsilon_{n,j=l\pm(1/2)}^{\mathrm{ref}}\}_{n,l}$, respectively, which is not ensured at all in practice. Since shape-consistent PPs are extracted from the ground-state configuration, the transferability to the excited states has to be checked.[10] Therefore additional numerical investigations would be required to compare both shape-consistent two-component and our new uncontracted SO-CI-adapted implicit hybrid one-component extraction procedures.

VII. CONCLUSION

The recently proposed hybrid one-component extraction procedure of the spin-orbit pseudopotential has been adapted to uncontracted SO-CI calculations in order to avoid any double counting of the valence spin-orbit polarization and relaxation effects. Two solutions were investigated. The first

one, called "explicit method," uses a reference all-electron four-component Dirac-Coulomb spin-orbit CI in order to calculate explicitly the valence spin-orbit polarization and relaxation effects. Due, in particular, to the well-known "pseudovariational collapse" which occurs in valence-only four-component spin-orbit CI calculations, this method turned out to be cumbersome. The second solution, called "implicit method," consists in extracting the SOPP at the SO-polarized and -relaxed CI levels. The atomic results on iodine demonstrate the validity of this approach for an accurate treatment of the SO interaction via a one-component PP calculation. Nevertheless, if high accuracy is desired in the pseudopotential computation of the spin-orbit coupling, the two-component extraction is found to be more suitable. But, in this case, the spin-orbit CI space has to be carefully chosen in order to calculate properly the valence spin-orbit polarization and relaxation effects as well as the fine-structure correlation ones.

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